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Are Published Minimum Vapor Phase Spark Ignition Energy Data Valid?

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Kirk J Staggs[1], Norman J Alvares[2], Daniel W Greenwood[3]

Introduction

The use of sprayed flammable fluids as solvents in dissolution and cleaning processes demand detailed understanding of ignition and fire hazards associated with these applications. When it is not feasible to inert the atmosphere in which the spraying process takes place, then elimination of all possible ignition sources must be done. If operators are involved in the process, the potential for human static build-up and ultimate discharge is finite, and it is nearly impossible to eliminate.

The specific application discussed in this paper involved the use of heated Dimethyl Sulfoxide (DMSO) to dissolve high explosives (HE). Search for properties of DMSO yielded data on flammability limits and flash point, but there was no published information pertaining to the minimum energy for electrical arc ignition. Due to the sensitivity of this procedure, The Hazards Control Department of Lawrence Livermore National Laboratory (LLNL) was tasked to determine the minimum ignition energy of DMSO aerosol and vapor an experimental investigation was thus initiated.

Because there were no electrical sources in spray chamber, Human Electro-Static Discharge (HESD) was the only potential ignition source. Consequently, the electrostatic generators required for this investigation were designed to produce electrostatic arcs with the defined voltage and current pulse characteristics consistent with simulated human capacitance. Diagnostic procedures required to insure these characteristics involve specific data gathering techniques where the voltage and current sensors are in close proximity to the electrodes, thus defining the arc energy directly between the electrodes. The intriguing finding derived from this procedure is how small these measured values are relative to the arc energy as defined by the capacitance and the voltage measure at the capacitor terminals. The suggested reason for this difference is that the standard procedure for determining arc energy from the relation; $E = 1/2CV^2$ does not account for the total capacitance and impedance of the system.

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Background: Dissolution Project

As a matter of policy it is necessary to dismantle tactical weapons to ensure their safety and reliability. Similar dismantling procedures are employed obsolete to retire units. During this process the HE must be removed from critical components by dissection or by dissolution processes. , However dissolution processes require the application of combustible solvents. One unique dissolution project involves the use of heated DMSO.

The known properties of DMSO are listed in table 1. [1] Because of its low vapor pressure, no published data of minimum electrical arc ignition energy (M_i) was found.

Physical-Chemical Data for DMSO

Parameter	Value
Melting Point, T_m	18.55°C (65.4°F)
Boiling Point, T_b	189°C (372°F)
Flash Point, T_f	95°C (203°F)
Auto Ignition, T_a	300-302°C (572-576°F)
Lean Limit Conc, C_{LL}	3.0-3.5% volume
Rich Limit Conc, C_{RL}	42-63% volume
Lean Limit Pres., P_{LL}	22.8-26.6 mmHg, computed
Rich Limit Pres., P_{RL}	319-479 mm Hg, computed
Lean Limit Conc, C_{LL}	95.8-111.8 g/m3, computed
Rich Limit Conc, C_{RL}	1342-2013 g/m3, computed

Table 1

The dissolution process employs a specially designed glove box fabricated with a ventilation system designed to maintain a negative pressure within the box during all phases of operation as shown in (figure 1). A pneumatically powered reticulating pumping system is used to spray the DMSO through ring like manifolds with rows of spray nozzles directed inwards toward the HE and associated components. The DMSO is heated to 150°F by pumping it through a heat exchanger that used hot water as the heating medium. The glove box, ventilation system, manifolds, and supporting hardware were electrically bonded to minimize electrostatic charge development during spraying cycles.

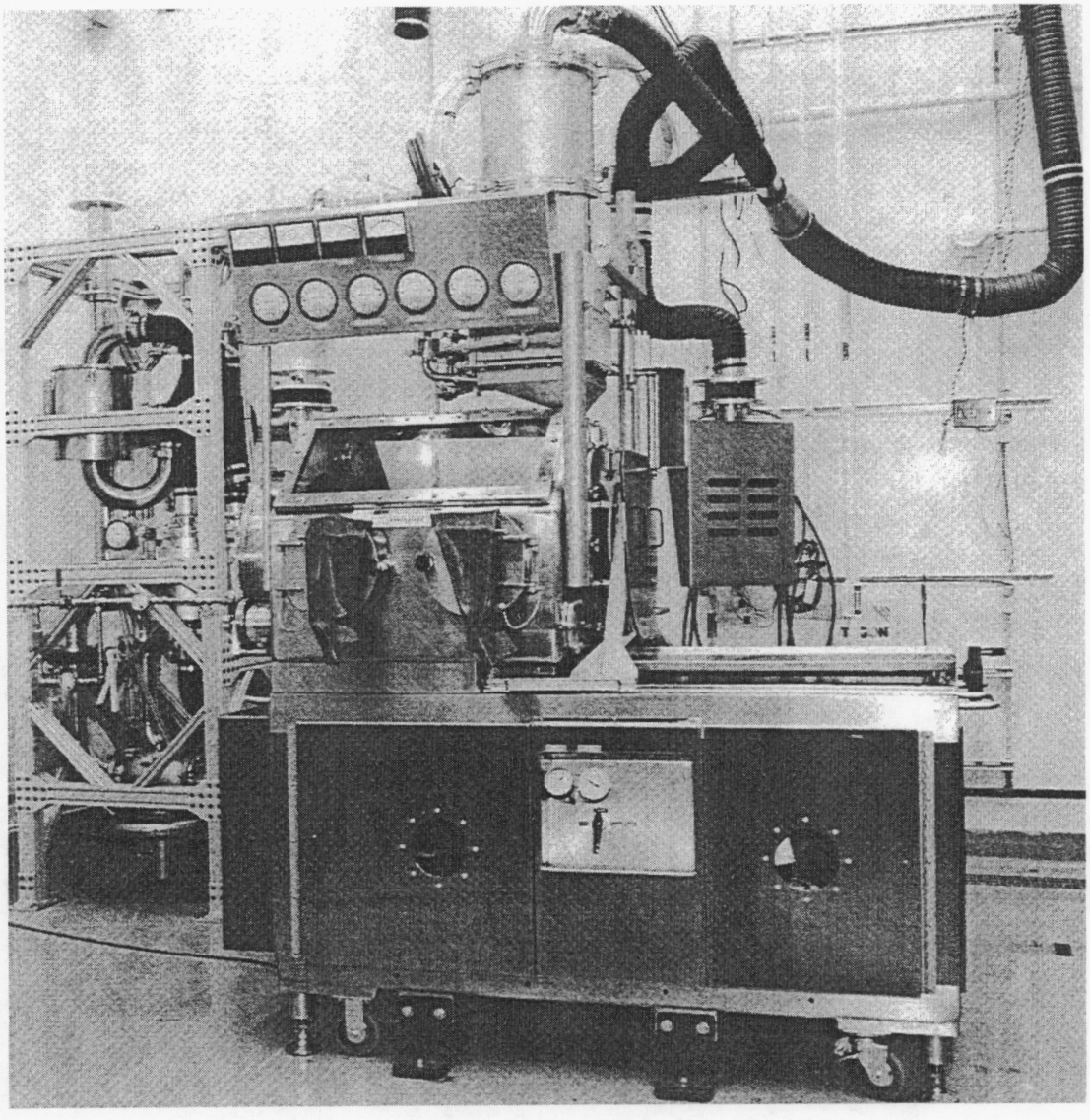


Figure 1. Dissolution Workstation

At selected interval during the dissolution process the manifolds were systematically moved to provide complete coverage of the HE. These adjustments are performed manually by accessing the glove box through the glove ports. Specified procedures mandate that the pump is to be turn off, the mist from the spraying action allowed to clear, and that operators bond themselves to the glove box prior to reaching into the box via the attached gloves. Initially however, there was resistance to bonding the operator because of procedural control issues and the difficulties performing the work while wearing bonding straps.

During development of the dissolution station safety studies predicted that arcs from electrostatic discharge (ESD) were extremely unlikely because of the engineered

electrical bonding and the conductive nature of DMSO. However, without bonding operators there was concern that ignition of the DMSO spray could result from HESD. Thus, to meet necessary safety criteria the minimum ignition energy ignition had to be defined.

ESD and HESD Ignition Study of DMSO Spray

An extensive series of tests were conducted to evaluate the minimum ignition energies for spray aerosols of DMSO and DMSO/HE solutions from HESD electrical arcs. [2] Tests were conducted in a metal glove box shown schematically in (figure 2).

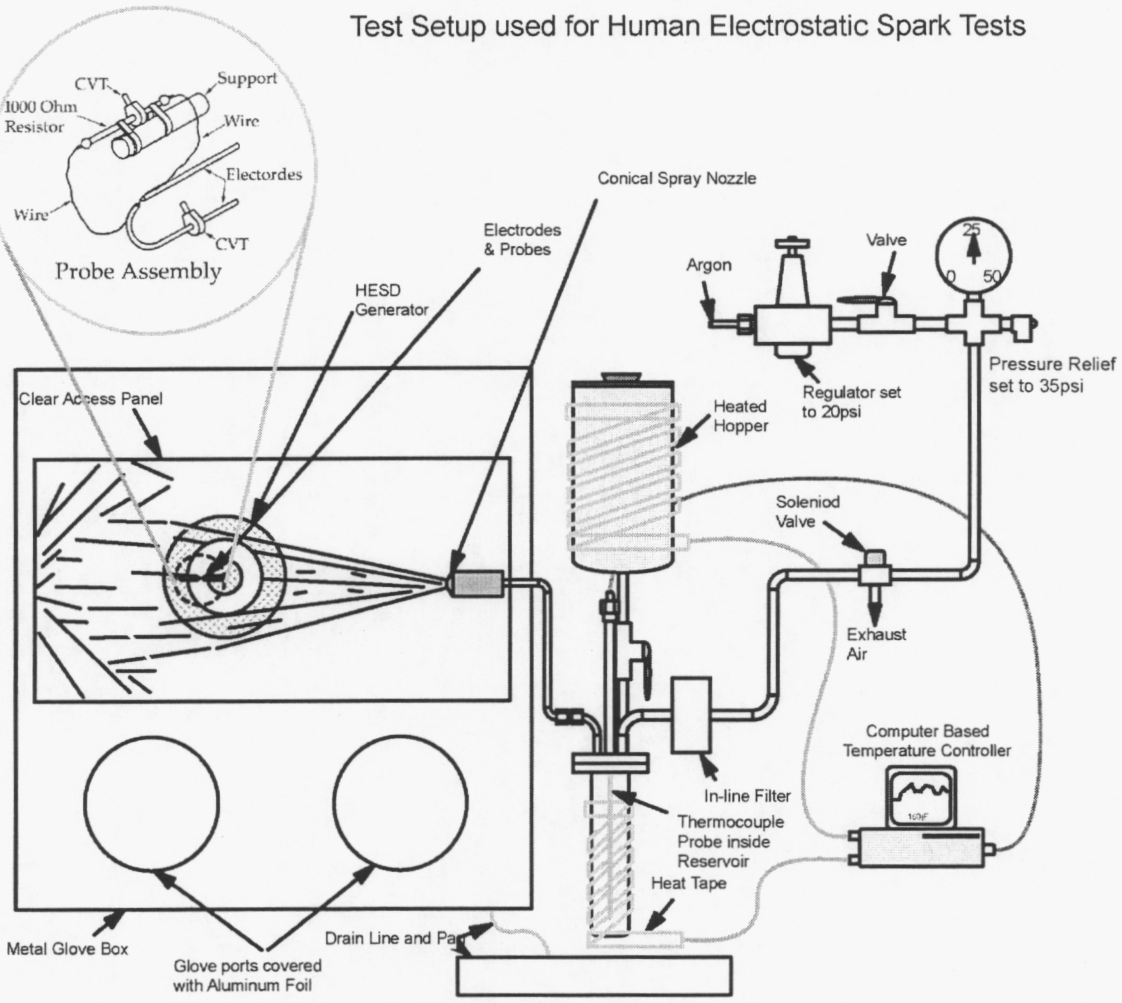


Figure 2

The following parameters were controlled:

- DMSO flow rate and delivery pressure
- DMSO aerosol distribution and particle size range
- DMSO temperature
- Spark generator stored ignition energy
- Ambient room temperature
- Glove box temperature

Two types of ESD generators were used as a source for the arc energy in this study. One of the generators, obtained form Sandia National Laboratory (SNL) call the Sandia Severe Human Body electrostatic Discharge Tester (SSET), could provided arc energy levels up to 7 milli-joules (mJ). However, this unit was designed to evaluate the effect of ESD on electrical components and was not adequate for developing the power levels of electrical arcs required for ignition studies. In addition, tests were conducted at Combustion Research Center to determine spark ignition profiles for DMSO vapors at elevated temperatures [3]

The energy produce within an electrical arc is primarily a function of the circuit resistance, capacitance, and the medium that the arc transverses. The difference between ESD and HESD is the resistance of the human body. LLNL developed an ESD generator that closely simulates the charge capacitance and resistance of a human body. The initial design consisted of ceramic capacitors, resistors, and a EGG high voltage Gap switch in a small cylindrical package. This package was placed behind a test chamber and attached to electrodes inside the chamber using high voltage cable commonly used for pulse power systems. The probes used to measure current and voltage were mounted on the backside of the test compartment. However, this configuration produced questionable results that indicated a significant difference in the stored energy and the measured results. To address this issue, independent electrical analysis was conducted by the pulse power systems group at LLNL to study the electrical arc energy and the stored energy within the system. Based upon these studies, a determination was made to minimize or eliminate the cable between the generator and electrodes and to install the current and voltage probes as close as possible to the end of the electrodes. [2]

A photo of the final design is shown in (Figures 3) with the unit attached to the back wall of the test chamber. Aluminum disks that support internal components were also use as electrical conduits. One electrode was directly attached to the aluminum disk attached to the test chamber and the other electrode was directly attached to the EGG Gap switch. This eliminated the need for cables between the generator and electrodes.

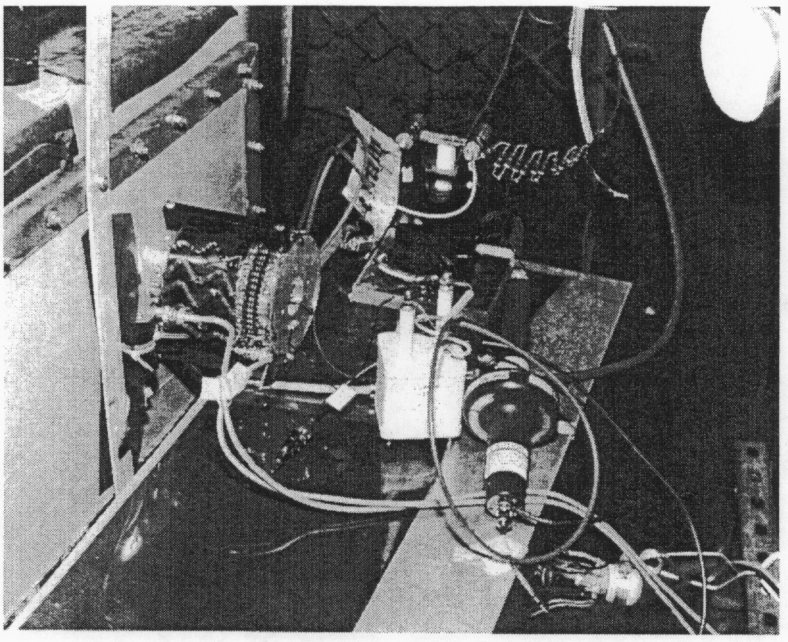
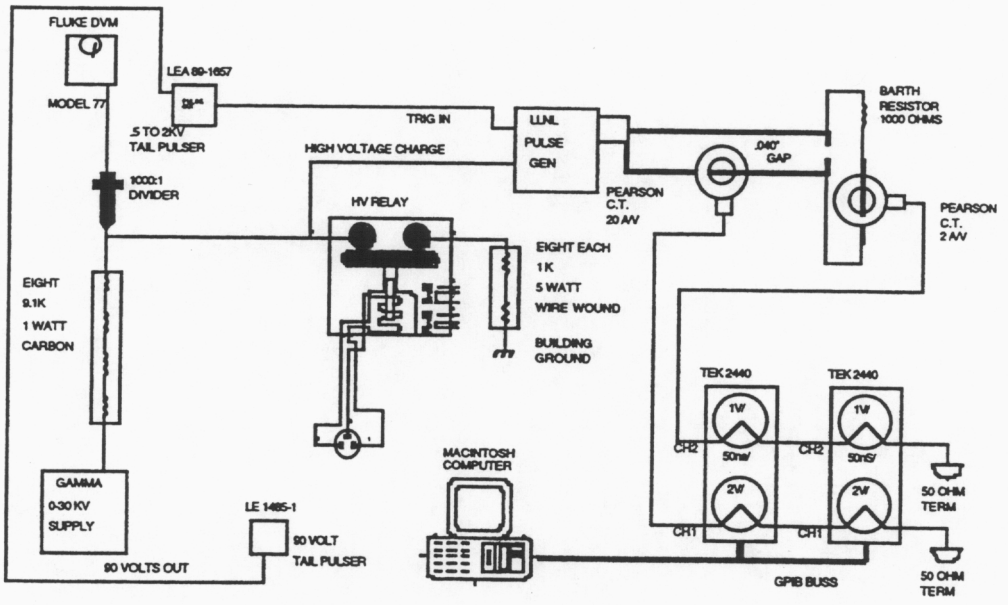


Figure 3

A schematic of the HESD generator circuit showing the generator components and probes is shown in (figure 4).



LLNL GENERATOR EXPERIMENT SET UP

Figure 4

The two electrical parameters measured were the voltage across the arc gap and the discharge current. Since the arc voltage rise time is relatively fast (on the order of 5 to 10 nanoseconds), series resistance and inductive components presented by the leads connecting the arc gap to the pulse source will adversely affect the measurement. A ground reference for this measurement would involve very high common mode voltage and introduce the possibility of ground loops. To address these problems a floating voltage probe was used with a connection as close to the arc gap as possible. The arc voltage was impressed across a Barth 1 Kilo-ohm high voltage resistor with known response and voltage vs. resistance coefficient characteristic. A Pearson current transformer (model 2877, 0.5 volts/ampere, 2 nanosecond response, 1% accuracy) was then used to measure the current in the 1 Kilo-ohm resistor. The normal sensitivity of this probe configuration was:

Resistor: I = 1 kV/1K Ω
Current Transformer: I = 2 amperes/volt (when terminated in 50 ohms)
Probe System: Ep = 2 kV/volt

The arc discharge current measurements were made using another Pearson current transformer (model 2878, 5 ns response, 0.05 volts/ampere, 1 % accuracy). Since the current in a series circuit is common to all elements, the current transformer can be placed in any location in the discharge circuit. The nominal sensitivity of this probe was 20 ampere/volt.

Both the arc voltage probe and the circuit current probe were attached to a Tektronix 2440 transient digitizers oscilloscope, which captures the signal voltage from the probes. These transient digitizers have a minimum rise time of 3 nanoseconds and a maximum sample rate of 2 nanoseconds per point. A computer and custom written LabView application provided transient digitizer control and raw data collection.

The recorded voltage was converted to the appropriate arc gap voltage and current. Any baseline shift was removed from raw current and voltage data to normalized each waveform to an initial zero. Voltage and current waveforms were multiplied to generate power in watts. This power waveform was trimmed to provide limits for the energy derived from the resulting area under the power curve according to equation (1) below.

$$E = \int_0^t (vi)\ dt \qquad (1)$$

Where v is the spark gap voltage and i is the current at time t.

(Figure 5) show an example of the voltage and current waveform recorded during the arc process. In this example the voltage builds up on the ends of the electrodes to 6000v before ionizing the air in the gap between the electrodes. At point (t=0) the current flow starts to increase, the resistance across the electrode gap drops and the voltage drops.

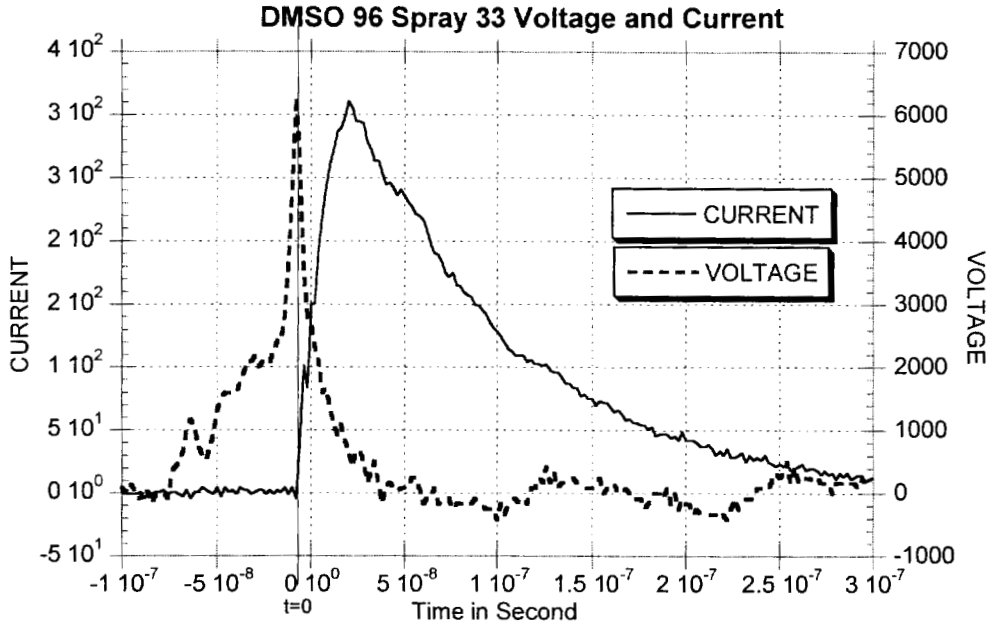


Figure 5

(Figure 6) show the curve of the power derived from the voltage and current from point t=0.

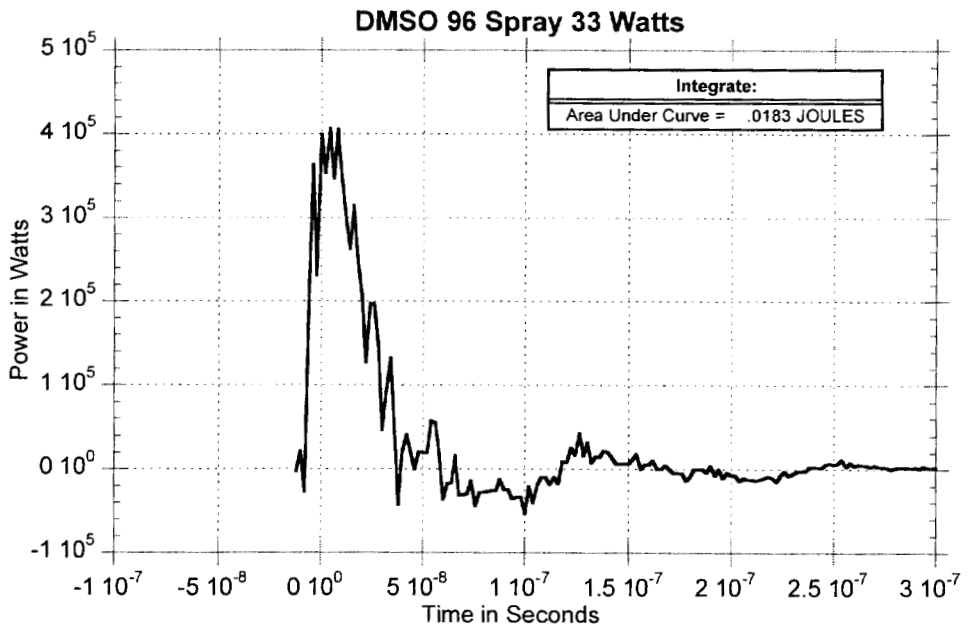


Figure 6

The current/voltage transformers (CVT) have a specified accuracy of one percent with a usable rise time of two or five nanoseconds depending on the model. They were

calibrated using a Tektronix PG508 pulse generator with a 5 nanosecond rise time, a Tektronix 2465 oscilloscope with a 1.16 nanosecond rise time, and a HP 3458A multimeter. The connecting cables used during calibration were the same used for the experimental runs. Any rise time and bandwidth losses were a part of the calibration when these cables were used. The results of the calibration achieved two percent accuracy in voltage and current probes. The voltage probe had a calibration value of 2084 volts per volt. The current probe had a calibration value of 21.6 amps per volt.

The Tektronix 2440 transient digitizer calibration was verified to one half of one percent. Voltage steps from zero to five volts were applied to the input and simultaneously monitored on the HP 3458A multimeter. The data values were then input into a LabView routine that calculated Mean Squared Error and Slope. The accuracy of these data using this procedure was 0.45%.

The test parameters and results are summarized in Table 2. Minimum ignition energy of the DMSO spray obtained with the LLNL/HESD unit ranged between $15mJ \leq M_i \leq 18mJ$. This range is substantially greater than the highest credible HESD arc of 7mJ. Review of the data reveals the interesting observation that there is a significant difference between the stored energy and the energy measured within the arc, i. e., the stored energy calculation averaged 15 to 17 times more than energy measured at the spark gap by the LLNL/HESD unit. This is interesting because the current standard (ASTM E-582) determines M_i in gases and vapors by calculating $E=1/2\ CV^2$, Where C is the capacitance of the system capacitor and V is the stored voltage.

Test	% by wt: DMSO	% by wt: HE	Atmo-sphere	Generator Voltage	Spark Energy mJ	Calc Energy mJ	Number of Ignitions	No. of Sparks per ignition	Comments
19	100.0		Air	10-13KV	est. >20	100 -170	3	5, 3, 1	LLNL Gen w/ 2nf Cap
20	100.0		Air	18KV	?		0	10	LLNL Gen w/ 1nf Cap
21	100.0		Air	19KV	?		0	10	LLNL Gen w/ 1nf Cap
22	100.0		Air	30KV	3.1	212	0	10	Sandia's gen w/470pf cap
23	100.0		Air	30KV	6.5	212	0	21	Sandia's gen w/470pf cap
24	75.0	25.0	Air	30KV	5.7	212	0	29	Sandia's gen w/470pf cap
25	100.0		Air	20KV	>13.0	200	0	12	LLNL Gen w/1nf Cap
26	100.0		Air	20KV	26-29	400	3	8, 1, 5	LLNL Gen w/ 2nf Cap
27	100.0		Air	12KV	8.6	144	0	21	LLNL Gen w/ 2nf Cap
28	100.0		Air	15KV	?	225	multiple	unknown	LLNL Gen w/ 2nf Cap
29	75.0	25.0	Air	12KV	8.8	144	0	13	LLNL Gen w/ 2nf Cap
30	75.0	25.0	Air	12KV	8.3	144	0	13	LLNL Gen w/ 2nf Cap
31	100.0		Air	15KV	15	225	0	17	LLNL Gen w/ 2nf Cap

Table 2. Test conditions for spray ignition tests

Vapor Ignition Study

The ignition propensity of DMSO vapor at elevated temperatures were surveyed using a modified version of the Bureau of Mines ignition apparatus. This apparatus is similar to the unit described in ASTM E-582. The procedure was to inject a small quantity of the

DMSO liquid into a container heated to slightly less the test set point temperature. The temperature of the container was then heated to the set point and the internal atmosphere stirred to insure appropriate mixing. The pressure in the chamber was reduced to 664 mm Hg to simulate negative pressure conditions in the workstation and ignition of the mixture was attempted over the temperature range of interest. The open cup flash point for DMSO, from table 1 is 95° C (203° F). Thus, ignition response was not expected at temperatures below the flash point

Using two strong ignition sources, (a chemical match of approximately 130 J nominal energy and a carbon electrode spark unit of approximately 60 J nominal energy) the lower flammability temperature limit (LFL) of DMSO vapor was found to be 79° C (173° F) and 81° C (178° F) respectively. Positive determination of ignition was indicated by excessive pressure rise in the chamber. (Figure 7) shows these data.

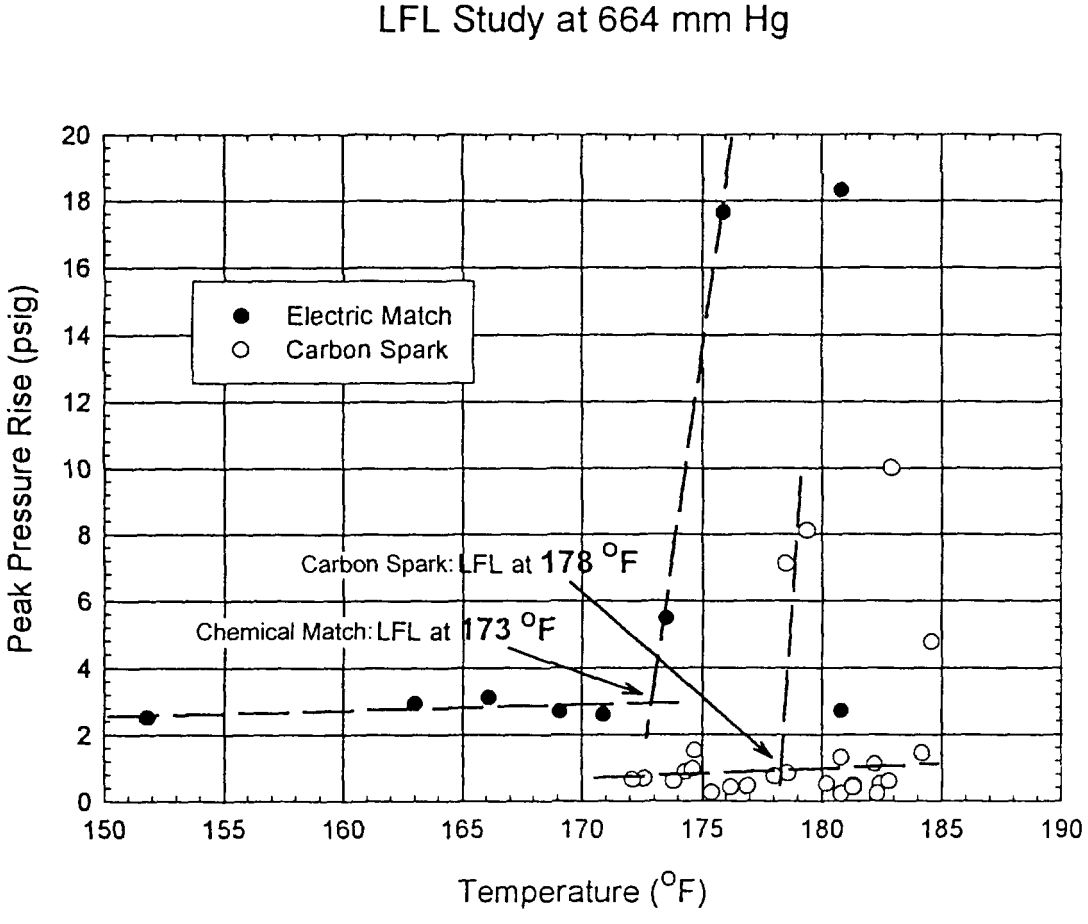


Figure 7

Nominal ignition energies of heated DMSO vapor at increasing temperatures were then determined using two pointed graphite electrodes separated by a 3 mm gap. (Figure 8) plots the nominal ignition energy (mJ) vs the DMSO vapor temperature. It is interesting

to note that at the temperature of the published DMSO flash point, the nominal ignition energy is above 10 mJ, which is 3 mJ above the maximum potential HESD of 7 mJ. The pressure in which these tests were conducted was about 0.9 bar. Consequently, the measured ignition energy should be approximately 10 % higher than the ignition energy at 1.0 bar. However, the data trends should be conserved. Note that the nominal ignition energy calculations are determined using the system voltage and capacitance at electrode gap break over. The actual spark energy of the discharge could be a tenth or less of this value, based on considerations from the spray ignition tests.

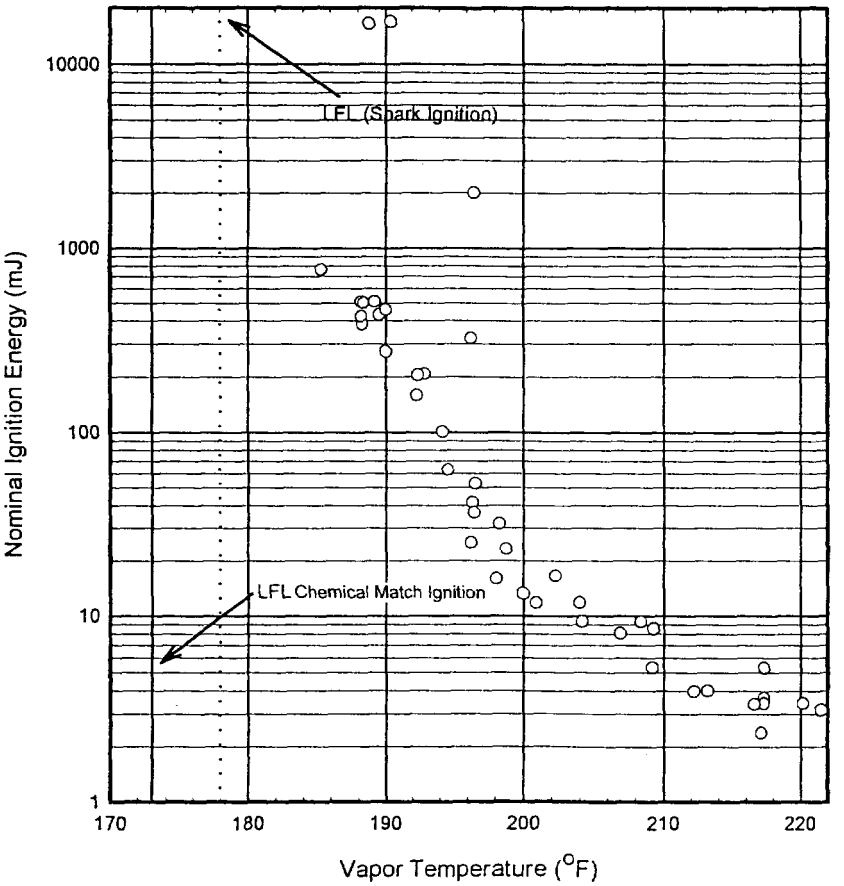


Figure 8

Current Standard Minimum Ignition Energy Measurements of Gases and Vapors

The American Society For Testing and Material (ASTM) standard E-582, "Standard Test Method for Minimum Ignition Energy and Quenching Distance in Gaseous Mixture", uses a high voltage power supply to charge capacitor(s) that are in parallel with the electrode circuit shown in (figures 9a and 9b). The process involves setting a gap between electrodes and slowly charging the capacitor of a measured or known value until the potential across the capacitors and electrodes reach the break over point of the arc gap. When break over occurs the capacitor discharges its stored energy to the electrodes and across the gap until the voltage drops to a level that will no longer sustain an arc. An isolation resistor limits the amount of current available from the power supply to limit the

arc duration. To determine spark energy, the voltage potential developed on the electrodes, which represents the charge voltage on the capacitor, is measured and recorded at break over and the ignition energy is calculates using the formula $E = 1/2\ CV^2$. This standard states that the reproducibility and presumed accuracy of M_i is ±10%.

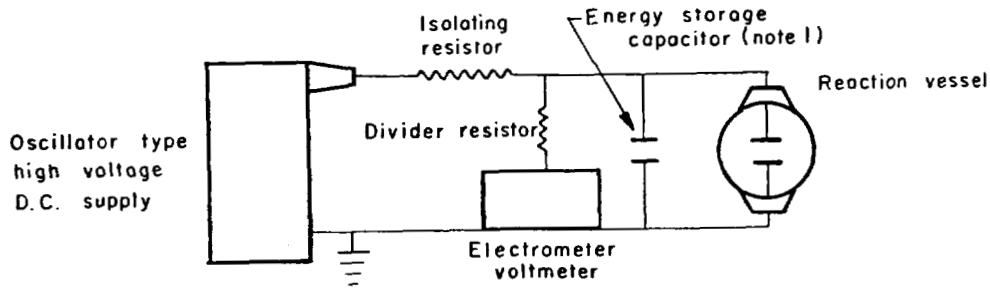


Figure 9a

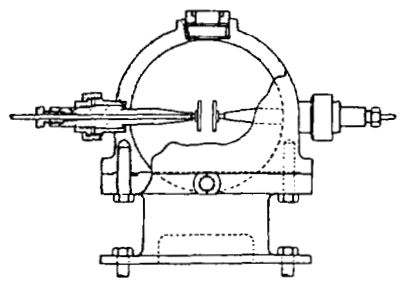


Figure 9b

There are many different factors that can influence the accurate determination of M_i, particularly in heterogeneous mixtures such as sprays and dust distributions. In fact, it has been acknowledged that it is very difficult to define M_i for systems where air velocity and turbulence must be high to maintain levitation of aerosols. [4] For fluids of low vapor pressure such as DMSO, flammable concentrations of vapor can only be developed at elevated temperatures. Apparatus design can also influence the measurement of M_i: Electrode size, shape, presence of quenching flanges and composition influence the discharge efficiency. The resistance, inductance and capacitance of the circuit elements can markedly modify the total power to the electrode tips. The diagnostic equipment can directly impact the accuracy and precision of the data. Results from the LLNL/HESD ignition tests for DMSO show that the apparatus design and diagnostic procedures have a significant and large effect on determination of the magnitude and temporal character of energy delivered to the spark gap. The order of magnitude difference between measured M_i and M_i calculated from $1/2CV^2$ calls to question the data produced by current standard methods.

Historical Minimum Spark Ignition Data

Tables that list M_i data are found in handbooks, monographs, standards and reports that focus on the subject of fire and explosion. [5-10] The lists are generally collections of data from research published in journals or symposium proceedings. Some of these data for selected flammable gases and vapors are listed in Table 3. The first column of this table is from [5], Calcote, et al, and lists M_i data for a wide variety of flammable vapors and gasses. These data were determined at the stoichiometric fuel/air ratio to reduce the experimental time required to establish the true M_i, which, for most hydrocarbons occur at mixtures that are slightly richer than stoichiometric. The Apparatus used to produce these data was designed at the Bureau of Mines and is essentially the same as the unit recommended in the current ASTM E 582-86.

Table 3 Minimum spark ignition energy data from various sources

Fuel	mJ	mJ	mJ	mJ	mJ	mJ
Acetaldehyde	0.38	0.376	0.38		0.38	0.37
Acetone	1.15	1.15	1.15		1.15	1.15, (0.41)
Acrolein	0.137	0.137	0.175			0.13
Benzene	0.55	0.55	0.55	0.22	0.22	0.2
Carbon Disulfide	0.015	0.015	0.015	0.01-0.02	0.015	0.009
Ethane	0.285	0.285	0.42 (0.24)	0.24	0.25	0.24
Heptane	0.7	0.7	1.15, (0.24)			0.24
Hydrogen	0.028	0.02	0.02, (0.018)	0.019	0.017	0.016
Methane	0.47	0.47	0.33, (0.29)	0.29	0.3	0.21, (0.30)
Propane	0.31	0.29	0.305	0.25		0.25, (0.48)
Toluene					2.5	0.24
	Calcote, et al, Spark Ignition Effects of Molecular Structure. Ind. And Eng. Chem. 44, #11, 1952	Fire Protection Manual for Hydrocarbon Processing Plants, Vol 1, 3rd Ed. 1985. Most recent reference; Same as " C"	Report 1300, Basic Considerations in the Combustion of hydrocarbon Fuels with Air. NACA 1957	Loss Prevention in the process Industries, Vol 1, Frank P. Lees, Butterworths, London1989. Most Recent Reference, Burgoyne 1965, Factory Mutual Engineering Corp. 1967.	NFPA 53M, Oxygen Enriched Atmospheres, 1990. Most recent reference; Litchfield, Kuchta, Furno; Flammability of Propellant Combinations. Bureau of Mines Explosive Research Report 3997, 1966	Electrostatic ignitions of fires and explosions, Thomas H. Pratt; 1997. Burgoyne Inc. Marietta, GA. Most recent reference; Brittkon, L. G., Plant/Operations Progress, Vol 11, 1992.

Columns 2 through 5 [6– 9] list M_i data from collections that postdate Reference 5. The data in these columns are, for the most part from [5], or are determinations made from an ignition apparatus essentially identical to the Bureau of Mines design. Two sets of data for Ethane, Heptane, Hydrogen, and Methane in column 3 are listed because they include measurements using either; different electrode configuration, spark duration, electrode composition or fuel/air ratio. The data in Column 6, [10] are from measurements at

fuel/air mixture ratios that reflect the true minimum spark energy defined by the ignition apparatus. These data generally indicate M_i magnitudes lower than ignition values at the stoichiometric fuel/air ratio. These data were collected from a paper published in 1992, which we assume to be from measurements more current than data listed in the rest of table 1. Background materials in of the monograph indicate that the method used to determine M_i was similar to the method described in the current standard.

In most circumstances, the conditions of accidental electrical discharge are such that the released energy is more than adequate to cause ignition of released flammable gases and aerosols. Because of this fact, accurate information about M_i is not a requirement but intrinsically designed safety systems and components are mandated to insure safe operations in areas defined as "hazardous locations" Sources of electrical energy that are not easily controlled are caused by static processes such as HESD, which can occur because of a broad set of circumstances where charge separation is possible. There are also unguarded, low voltage, systems that are contained in systems containing flammable vapors and aerosols where the circuit characteristics are assumed to either preclude the possibility of electrical discharge or the where the discharge energy is considered to be safely below M_i for the environment. For this set of circumstances, accurate knowledge of M_i is a requirement to insure safe operations.

It is safe to assume that the historical M_i data from the references to table 3 were determined by the classical procedure of calculation using measured values of capacitance and voltage. Moreover, the consistency of the data in table 3 suggests that data in the more recent tables are, except for Reference 10, clones of the original work. [5] It is also an established fact that the technology of electrical measurement has vastly improved over the period since Reference 5 was published. The data produced during the DMSO spray tests using the LLNL/HESD unit provide some indication of the improvement in measurement and analysis of spark discharge energy. Indeed, (figure 10) is a curve that contrasts the difference in spark ignition energy values determined by measurement and by dependence on the stored energy calculation. It shows that the M_i calculated is 15 times M_i measured. Though this data is for a much more complicated fuel spray system at elevated temperatures, the trend is certain and should be conserved in standard gas and vapor phase environments. For these reasons we ask " Are published minimum vapor phase spark ignition data valid? And shouldn't these measurements be revisited to insure that they reflect accurate safety limits.

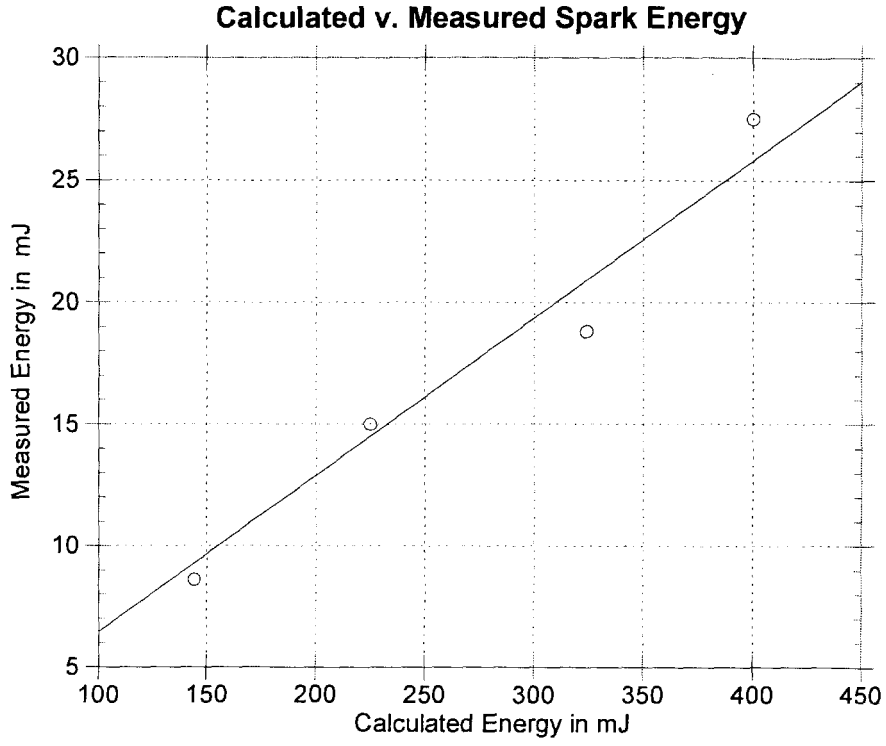


Figure 10

Conclusions

- Minimum ignition energy for heterogeneous DMSO sprays of particle size ranging from 0.08um to 0.4 um and aerosol concentration of 9.4 g/m^3, at average temperature of 71° C (160° F) ranged between 15 mJ$\leq M_i \leq$18mJ.
- Minimum vapor temperature for high intensity spark ignition is 81° C (178° F).
- Nominal spark ignition energy at the published open cup flash point temperature of DMSO (95° C, (203° F)) is ~ 9 mJ. The actual spark energy is likely to be substantially less than this value.
- Spark energies measured at the electrodes of the LLNL HESD spark generator average one order of magnitude lower than the calculated system energy of ½ MV^2 for all of the DMSO spray ignition tests.
- Improvement in instrumentation have allowed for much better Mi measurements
- Current method of determining Mi does not provide accurate measure energy produced in the spark
- Publish Mi energy maybe higher than actual Mi arc energy

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